# "In Depth" visualisation of silicone deposition to understand and control the microstructure driving changes in the mechanical properties of fabrics

**Summary: A** synchrotron nano-X-Ray Fluorescence (XRF) technique has allowed imaging the depth of penetration of extremely low levels of silicone which could not be detected by benchtop SEM-EDX technique. In this programme we studied the depth of penetration of two silicones (Terminally substitute Amine Silicone/TAS and PDMS), we observed that both silicones penetrate the cotton thread and are absorbed by the fibre, while these silicone material remain at the surface for a polyester fibre. Polydimethylsilicone (PDMS) appears to deposit more efficiently as small drops whilst Terminal Amino silicone(TAS) deposits more effectively as larger drops. PDMS deposits better on polyester and TAS better on cotton. In the aqueous gel scenario PDMS and TAS show similar homogeneity, although the latter deposited slightly less.

**Background:** This study aims to understand the fundamental physics of deposition of silicones with various physical and chemical properties onto fabrics for breakthrough softness benefits. Critical to the delivery of such benefits is the understanding of the homogeneity of the deposition on the surface and depth of penetration into the fibres. We show how only synchrotron nano-X-Ray Fluorescence (XRF) technique has allowed imaging the depth of penetration of extremely low levels of silicone which were not detectable by benchtop SEM-EDX technique. This study combined with Friction, Bending and Compressibility testing (also known as the 3D consumer predictive feel model tool) the findings will bring new insights into the mechanics of how softness and fabric feel is imparted.

## Conclusions

- Both silicones penetrate cotton thread and are absorbed by the fibre, while remaining at the surface for polyester.
- Polydimethylsilicone (PDMS) appears to deposit more efficiently as small drops whilst Terminal Amino silicone(TAS) deposits more effectively as larger drops
- PDMS deposits better on polyester and TAS better on cotton.
- In the aqueous gel scenario PDMS and TAS show similar homogeneity, although the latter deposited slightly less

**Technical challenge**: So far the information available on fabric deposition is the total amount of the deposited silicones via extraction + ICP-AES as well as the homogeneity of the surface deposition via SEM-EDX. To gather information about the depth of penetration of the actives inside the fibres, we used a technique that works beyond the surface imaging and can detect extremely low levels of silicone deposit (< 10 μg/g fabric). Synchrotron nano-XRF technique is a unique tool for this purpose as its high sensitivity allows to selectively image a large range of elements using their x-ray fluorescence fingerprint. For the deposition of actives, we track selectively the Si atoms of the silicones. The fabric/active microstructure can be then correlated with the macroscopic mechanical properties (friction, bending and compression). Such mechanistic understanding will help in developing tailored silicone actives that interact selectively with the targeted fabrics in harmony with the rest of the formulation.

## Experimental method and detailed results:

**1)** Different solvent mixtures.

A key parameter in dispersions is the dispersed phase particle size. To obtain a range of drop sizes we used combinations of organic solvent to obtain silicone droplets in the sub-micron size range. Where edging closer to a theta solvent yields smaller silicone drops. Solutions of 300 ppm silicone were prepared in solvent composed of varying concentration of hexane in ethanol. The concentrations of the solvents range from 10 % to 100 % w/w. The particle size analysis of premixed silicone-solvent solutions was carried out using a Zetasizer light scattering instrument. The following figure shows size evolution as a function of solvent mix.
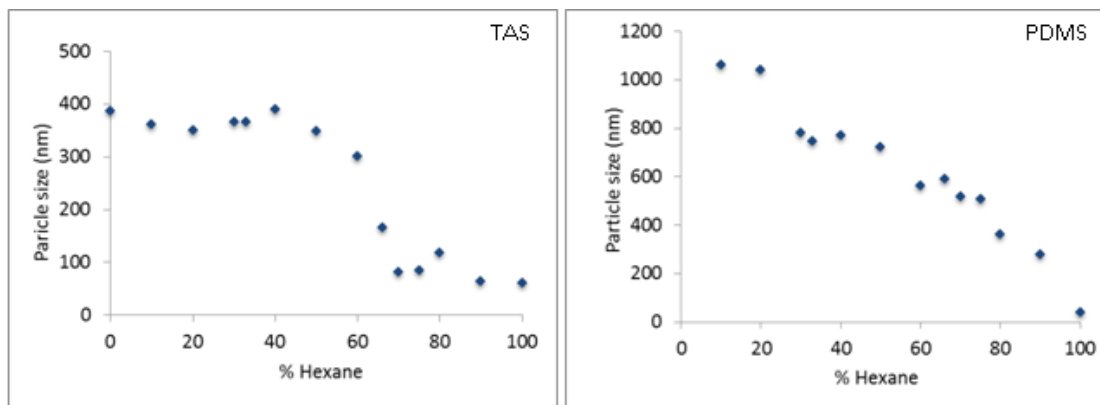


*Figure 1. TAS and PDMS droplet size at varying solvent ratios*

*2)* Deposition of actives

Fabric samples of Polyester and Flat Cotton were soaked in each corresponding treatment for 30 minutes at room temperature. For sizes on the micron range and comparison with a real system, we used an EFF-DA lamellar gel, within which the large drops are stabilised by the high viscosity of the gel. Dissolution of the gel leads to the release of these now unstable silicone drops which deposit on surfaces. The lamellar gels were prepared as previously reported at 40% w/w loading of PDMS and TAS.

## 3) Results,

### a: SEM/EDX

To carry out a preliminary assessment on the deposition of silicone, the fabrics were analysed in NIC Powder Characterisation Lab via SEM with EDX functionality. Below are a range of SEM images and EDX spectra clearly showing presence of Silicon on the fabrics.
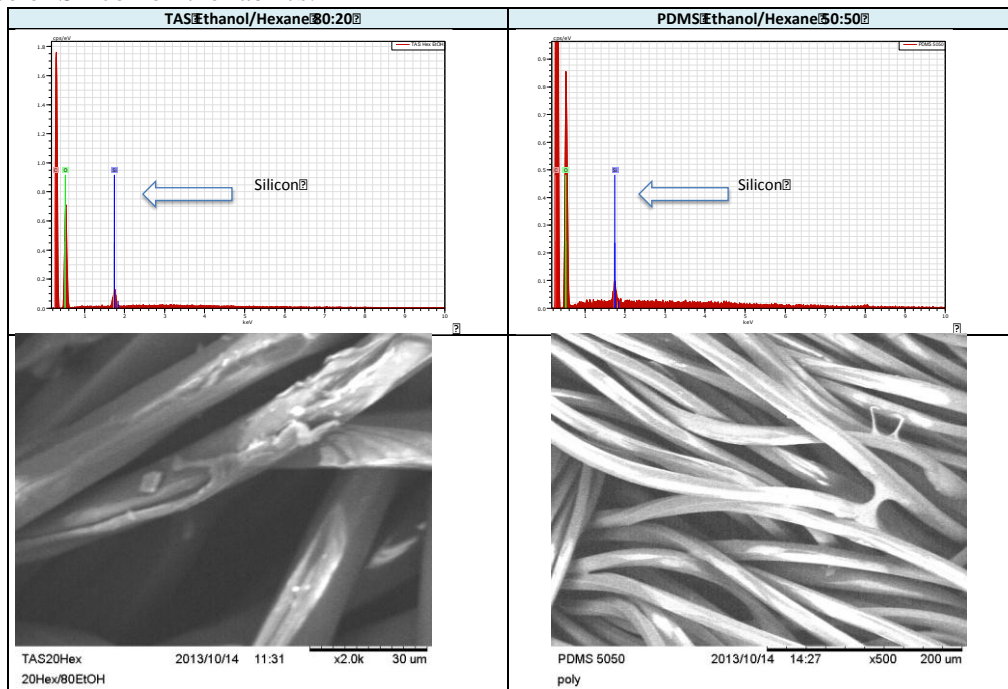


Figure 2. SEM-EDX

### b: Synchrotron Nano-X-ray Fluorescence

SEM-EDX does not allow getting information about the depth of penetration. To access it, we embedded the fibres covered with silicone into a resin and microtomed 10μm thick slices. We then have access to the full cross-section of the fibres that have been exposed to the actives. These slices were imaged by X-ray fluorescence to locate the silicone inside the fibres.
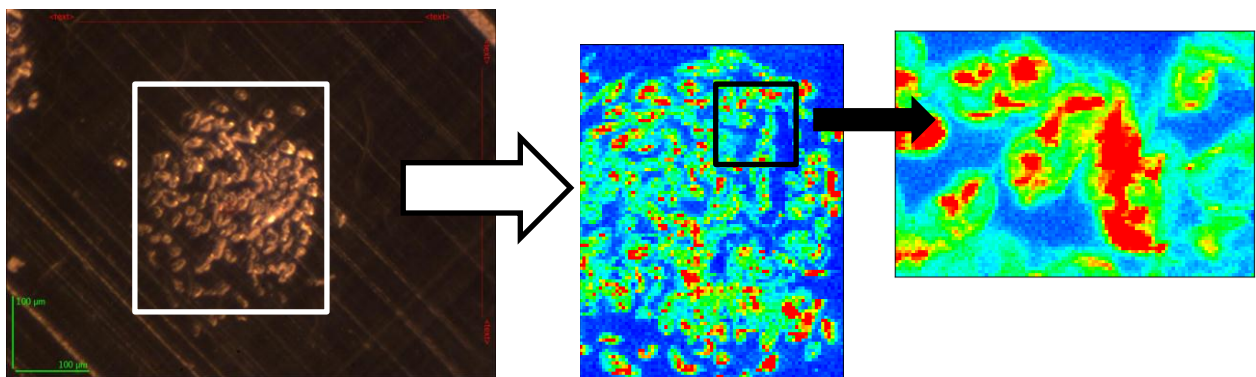


Figure 3. Nano-XRF experiment

Figure 3 shows the measurement sequence. We first observe our sample on the optical microscope and locate one yarn of interest (highlighted in white in the picture). This region of interest is then scanned point by point by a 3x3 μm beam to obtain the fluorescence image of a selected atom (Si in our case). The X-ray excites the Si atoms deposited and their fluorescence signal enables us to locate the actives. We finally use a 500nm x 500nm beam to obtain high resolution of selected fibres within the yarn.

The first insight is that **in any case, Silicone goes to the core of the cotton fibres while it stays on the outside for polyester**. Figures 4 shows this clearly at the highest resolution. The yellow and red zones (high amount of Si) are located in the core of the fibres for cotton when it is forming a shell around the fibre for polyester. Natural cotton fibres are more porous than extruded polyester fibres, explaining this difference in behaviour. This is a completely new insight that will help understand the softness mechanisms; cotton, by absorbing the silicone, might have better bendability, when polyester, by being covered with silicone, might have better friction profile. (3D model work in progress)



<div align="center">
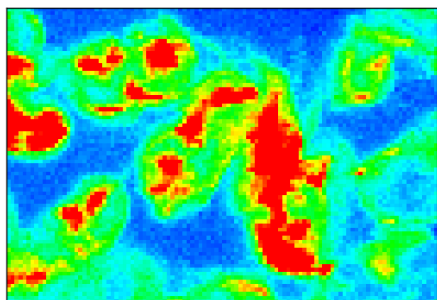
Cotton: Silicone inside
the fibres
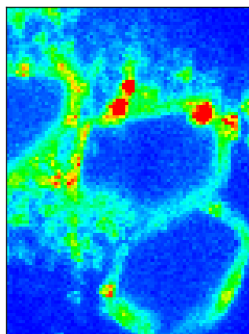
Polyester: Silicone around
the fibres

*Figure 4. XRF image of cotton and polyester fibres soaked in 100% hexane PDMS solution*

</div>

The effect of solvent polarity has then been investigated using the same approach. In figure 5 we observe that there is not much fluorescence for PDMS at the 80-20 EtOH-Hexane solvent mixture in cotton but a little more on polyester. At this solvent ratio, PDMS droplet is found to be ~1 µm which for that concentration may not lead to high density uniform deposition.

For fabrics treated in 100% hexane solutions the distribution and intensities appear similar for cotton and polyester. The PDMS droplet is now significantly smaller at ~50 nm.
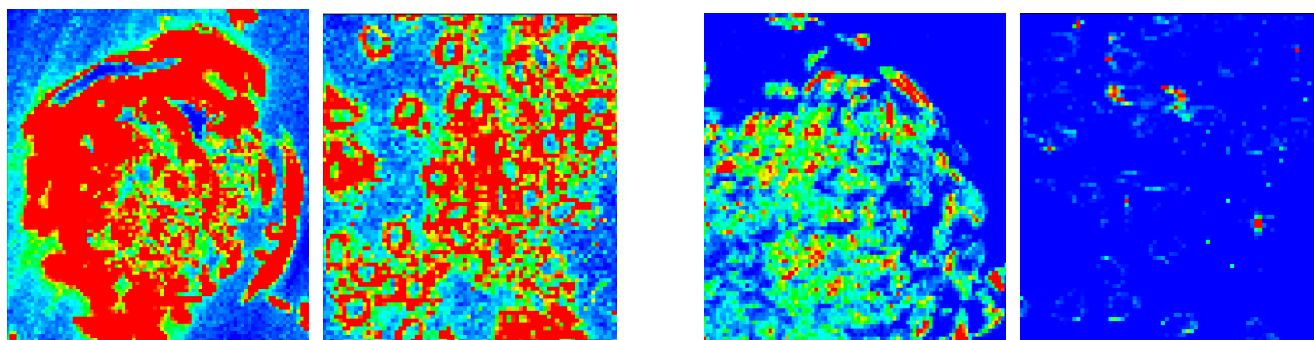


<div align="center">
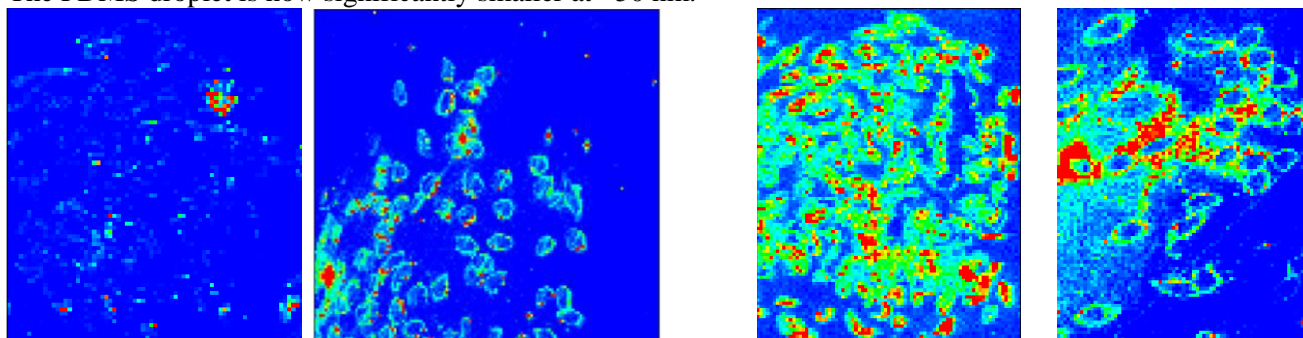
Cotton          Polyester

PDMS 80-20% EtOH-Hexane

Cotton          Polyester

PDMS 100% Hexane

*Figure 5. XRF images of cotton and polyester fibres soaked in PDMS solution in various solvent*

</div>

PDMS, being very hydrophobic, tends to deposit easier on a hydrophobic surface when in a 'bad solvent system' i.e higher Hexane content.

In the case of TAS, due to its different polarity, the picture is reversed, the lower hexane content solutions provides the highest levels of deposition. The particle sizes are significantly sub-micron at ~350 nm for 20% Hexane and ~50 nm for 100% hexane.



<div align="center">

Cotton          Polyester

TAS 80-20 EtOH-Hexane

Cotton          Polyester

TAS 100 Hexane

*Figure 6. XRF images of cotton and polyester fibres soaked in TAS solution in various solvent*

</div>

Figure 6 shows that unlike PDMS, when TAS is in a a good solvent, it tends to deposit more on the cotton fibres and almost not at all of polyester fibres. This can be explained by the fact that TAS is less hydrophobic than PDMS, hence is more attracted to cotton fibres.